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# Stability in bcc transition metals: Madelung and band-energy effects due to alloying

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## Abstract

The phase stability of the bcc Group VB (V, Nb, and Ta) transition metals is explored by first-principles electronic-structure calculations. Alloying with a small amount of a neighboring metal can either stabilize or destabilize the bcc phase. This counterintuitive behavior is explained by competing mechanisms that dominate depending on particular dopant. We show that band-structure effects dictate stability when a particular Group VB metal is alloyed with its nearest neighbors within the same d-transition series. In this case, the neighbor with less (to the left) and more (to the right) d electrons, destabilize and stabilize bcc, respectively. When alloying with neighbors of different d-transition series, electrostatic Madelung energy dominates over the band energy and always stabilizes the bcc phase.

The cohesion of the transition metals have long been assumed to be well understood arising from a gradual population of first bonding and later anti-bonding states as one proceed through the transition series [1]. This scenario nicely explains the parabolic behavior in atomic volumes and bulk modulus that reach a minimum and maximum, respectively, at the maximum of occupied bonding states near the middle of the series. The observed sequence of hexagonal-close-packed (hcp), body-centered-cubic (bcc), and face-centered cubic (fcc) crystal structures in the d-transition metals is a consequence of the occupation and characteristic shape of the d-band electron density of states [2]. For the 3d transition metals the sequence is slightly altered due to magnetism

that de-couples bands of different spin [3]. Thus, for the columns (V, Nb, and Ta) and (Cr, Mo, and W), and for Fe (magnetic), the bcc phase is stable due their particular d-band population. Complex structures, as those found for the early actinides (5f-transition metals), are ruled out for two fundamental reasons. First, the d-bands are not as narrow as the 5f bands and cannot sustain the Peierls-type of distortion taking place in the actinides and second, electrostatic (Madelung) interactions favors closer packed atomic arrangements with higher symmetry [4].

Recently, measurements on vanadium raise some doubts about the outlined conventional view of bonding in the transition metals. Namely, a new rhombohedral phase (*rh*) was discovered around 60-70 GPa in synchrotron x-ray diffraction measurements [5]. Later theoretical studies confirm this finding and also suggest vanadium to return to the bcc phase above about 300 GPa [6-9]. It has been proposed that the intra-band Fermi-surface nesting is responsible for this peculiar behavior [10, 11]. The instability of the bcc phase also appears to be associated with a substantial softening of the shear elastic constant  $c_{44}$  in vanadium with pressure. In fact, vanadium's Group VB relatives, niobium and tantalum, also show a similar but less pronounced softening of  $c_{44}$ , see Figure 1. For vanadium,  $c_{44}$  initially increases with pressure as to be expected for a stable phase, but close to 20 GPa it drastically decreases. We predict the phase transition to the *rh* phase at 60 GPa, close to the observed 60-70 GPa. For Nb a similar behavior is observed with the shear constant reaching a low minimum close to 50 GPa before rising again [10, 11]. In Ta the softening is less severe but found between 50-80 GPa, see lower panel of Figure 1. Recognizing the relationship between  $c_{44}$  and the *rh* phase in V, it is important to also investigate and understand possible structural instabilities in Nb and Ta as well.

In this Letter we aim to explore and explain the possibility of stabilizing or de-stabilizing V, Nb, and Ta by means of alloying with small amounts of members from the neighboring columns in the Periodic Table, namely the Group IVB (Ti, Zr, and Hf) and Group VIB (Cr, Mo, and W). To this end, we have applied density-functional-theory (DFT) first-principles techniques for the electronic structure. Specifically, the exact-muffin-tin-orbitals [12] method (EMTO) is applied within the coherent potential approximation [13] (CPA) for the best possible alloy treatment. The electronic structure

and total energy of random alloys are obtained from EMTO-CPA calculations that include the on-site screened electrostatic potential and energy for the charge transfer between the alloy components within the single-site (SS) DFT approximation [14]. The net charge on the alloy atomic sphere (charge transfer between the alloy components within the SS-DFT) and the values of the screening constants are obtained from the locally self-consistent Green function [15] (LSGF) calculations for 1024 atom supercell that models the random equiatomic V-M alloys (“M” is Ti, Zr, Hf, Nb, Ta, Cr, Mo, and W).

For comparison and analysis, we also perform all-electron full-potential linear muffin-tin orbital [16] (FPLMTO) calculations within the virtual crystal approximation (VCA), in which the alloy system is modeled by a fictitious metal with an atomic charge and valence corresponding to the concentration average between two neighboring elements. In this approach the only influence the alloying has is a change of the valence electron population and it thus isolates the effect to changes in the band energy.

First we consider pure vanadium metal. Here our calculations show a phase transition to the *rh* phase at 60 GPa that abruptly changes its rhombohedral angle close to 110 GPa before returning to bcc at 310 GPa. This rather unusual behavior was also detected in previous calculations for vanadium [6-9]. In Figure 2 we display the total energy (EMTO-CPA) as a function of the rhombohedral distortion for vanadium metal and its alloys with 5 at. % of Ti, Cr, and Nb. In this plot the atomic volume is kept at  $8.056 \text{ \AA}^3$  (the Wigner-Seitz radius  $S_{WS} = 2.35 \text{ a.u.}$ ) that corresponds to pressure  $\sim 240$  GPa. Notice that pure vanadium is unstable with respect to the distortion and alloying with a small amount of its left neighbor Ti increases the instability. Adding a small fraction of Cr or Nb, however, removes the rhombohedral phase for  $\sim 5$  at. % Nb and  $\sim 11$  at. % Cr (not shown). Further EMTO-CPA calculations predict that also Zr ( $\sim 3$  at.%), Mo ( $\sim 4$  at.%), Hf ( $\sim 5$  at.%), Ta ( $\sim 5$  at.%), and W ( $\sim 4$  at.%) completely stabilize the bcc phase of vanadium at all studied pressures.

Thus, from all d-transition metals in Group IVB, VB, and VIB, only Ti does not prevent the rhombohedral phase in V. It has been discussed in previous investigations [6-11] that the cause of the distortion is due to intra-band FS nesting that contributes to the band energy. This nesting is sensitive to the location of the Fermi level, i.e. the number of

valence electrons, which then explains why increasing (Cr) and decreasing (Ti) the amount of valence electrons in V stabilizes and destabilizes the bcc phase, respectively. Our VCA treatment for vanadium models precisely this effect and confirms the band-filling argument. If no other fundamental mechanisms are involved, one expects that alloying V with Zr (one less valence electron) and Mo (one more) should similarly destabilize and stabilize the bcc phase, respectively. Surprisingly, our calculations reveal that not only Mo but also Zr enforces the cubic phase in V. It therefore appears unlikely that FS nesting or other electronic structure effects, influencing the band energy alone, dictate the crystal structure for V-Zr or V-Mo. To better understand the nature of the rhombohedral phase and when it can be expected we perform additional CPA and VCA calculations to study the effects of alloying and pressure on the remaining Group VB metals, Nb and Ta. The results are summarized in Figure 3 that shows the relevant part of the Periodic Table. Here we show that Ti in V, Zr in Nb, and Hf in Ta have a destabilizing effect on the bcc phase as marked by the horizontal arrows. For all other combinations of alloying of the Group VB metals the opposite occurs (stabilize bcc).

In order to explain this puzzling behavior we have to go beyond the band energy arguments and take a closer look at electrostatic energy contributions. According to Ref. [12], the total energy ( $E_{tot}$ ) can be expressed as the sum of the electron gas kinetic energy ( $E_s$ ), the so-called intra-cell energy ( $E_{intra}$ ) that combines electron-electron and electron-ion energies, the inter-cell (or Madelung) energy ( $E_M$ ), and the exchange and correlation energy ( $E_{xc}$ ). Let us define  $E_{tot} = E_I + E_M$ , where  $E_I = E_s + E_{intra} + E_{xc}$ .

Table 1 lists the total-energy response ( $\Delta E_{tot}$ ) (and its contributions,  $\Delta E_I$  and  $\Delta E_M$ ) to a 1 % monoclinic deformation, used for the shear elastic constant  $c_{44}$  calculations [10, 11], calculated for V and the  $V_{95}Nb_{05}$ ,  $V_{95}Ti_{05}$ , and  $V_{95}Cr_{05}$  alloys at the atomic volume  $\Omega = 8.056 \text{ \AA}^3$  (same as in Figure 2). Negative value of the total-energy change indicates mechanical instability of bcc vanadium. Adding niobium to vanadium significantly increases  $\Delta E_{tot}$  thus indicating stabilization of the bcc structure in the  $V_{95}Nb_{05}$  alloy. Notice that the increase of  $\Delta E_I$ , which is mostly due to the band-structure effects, is rather insignificant and the main reason for stabilization of the bcc structure in the  $V_{95}Nb_{05}$  alloy is instead the electrostatic Madelung energy  $\Delta E_M$ . Vanadium alloyed with titanium reacts differently! Here  $\Delta E_{tot}$  decreases signaling a further bcc destabilization.

However, contrary to the V-Nb system, the change in the band energy plays the dominant role while  $\Delta E_M$  remains nearly constant (Table 1). Finally, for the  $V_{95}Cr_{05}$  alloy, again the band energy is dominant, now having the opposite effect, and the Madelung part remaining nearly the same. Consequently,  $\Delta E_{tot}$  increases and approaches zero with a near stabilization of the bcc phase. Adding about 6 more at. % of Cr in fact dictates the bcc phase for all pressures in vanadium.

As we mentioned above, small amounts ( $\sim 3$ -5 at. %) of 4d (Zr, Nb, and Mo) and 5d (Hf, Ta, and W) metals are enough to stabilize the bcc structure of vanadium. For these alloys the Madelung contribution plays a decisive role in the stabilization, as opposed to the V-Ti and V-Cr alloys where it is insignificant. This contrasting behavior is due to the inherent difference between 4d and 5d states compared to the 3d states. The former are more extended in space as are their corresponding charge distribution. Consequently, there is a larger charge transfer when V is alloyed with a 4d or 5d metal than with its neighbors Ti and Cr. In Table 2 we summarize the calculated charge transfers for V alloyed with the members of Group IVB, VB, and VIB. The larger charge transfers result in larger on-site Madelung energies [14] that favor higher symmetry (bcc in this case) structures. The changes in the band energy, mainly due to small shifts of the Fermi level in the V-Ti and V-Cr alloys, play the decisive role in destabilization (Ti) or stabilization (Cr) of the bcc phase. This then explains why a larger Cr content ( $\sim 11$  at. % Cr) is required to entirely remove the instability in V while only about 4 at. % is needed for any of the 4d- or 5d-metal dopands.

The band energy in terms of an intra-band nesting of the FS is also responsible for the pressure-induced shear softening in niobium at  $\sim 50$  GPa [10, 11] (Figure 1). Hence, there is an interest to explore the stability of bcc Nb with alloying. Here we undertake calculations of the energy change of pure bcc Nb, and its alloys with 4d neighbors ( $Nb_{95}Zr_{05}$ , and  $Nb_{95}Mo_{05}$ ) caused by 1 % of the monoclinic deformation. Calculations are performed at the atomic volume  $\Omega = 14.92 \text{ \AA}^3$  corresponding to a pressure of  $\sim 50$  GPa and the results are presented in Table 3. There are obvious analogies to the case of vanadium (Table 1) alloyed with its nearest neighbors in the Periodic Table (Ti and Cr). Small addition of zirconium to niobium decreases  $\Delta E_{tot}$  due to the band-energy contribution but not quite enough to destabilize the bcc phase. When increasing the Zr

content to about 10 at. % in Nb, our calculations suggests a weak destabilization of the bcc phase (not shown) consistent with the scenario for Ti-doped V. Also analogous to vanadium, the Madelung contribution is rather insignificant while the change in the band energy is driving the destabilization. Adding molybdenum to niobium causes the same effect that is observed in the V-Cr alloy, the band energy further favors the bcc phase while the Madelung contribution is insignificant. Negligible changes of the Madelung energy when Nb is alloyed with its nearest neighbors (Zr and Mo) are similar to what happens for V-Ti and V-Cr. The reason is, as we explain above, the small charge transfers and the correspondingly small changes of the Madelung energy for alloys of the same d-transition series. For Nb-Zr the charge transfer is 0.084 and for Nb-Mo the charge transfer is -0.081, compared to 0.077 and -0.070 (Table 2) for the 3d analogs (V-Ti and V-Cr).

To summarize, we have identified significant softening in the shear elastic constant for the Group VB metals with pressure. For vanadium the softening is associated with a phase transition to a rhombohedral phase close to 60 GPa while for Nb and Ta the bcc phase still remains stable at all studied pressures. The effect of alloying on the phase stability has been studied and two dominant mechanisms are recognized. First, the band energy tends to destabilize and stabilize the bcc phase when a member of the Group VB V (or Nb, Ta) is alloyed with its nearest neighbor from the *same* d-transition series to the left Ti (or Zr, Hf) and to the right Cr (or Mo, W), respectively. Second, the electrostatic Madelung energy removes softening and secures the bcc phase when a Group VB metal is alloyed with neighboring (Group IVB and VIB) elements from a *different* d-transition series. This finding is schematically displayed in Figure 3.

The instability and anomalous pressure-behavior of the shear elastic constant in the Group VB metals are not understood from the conventional bonding picture of the d-transition metals. Instead, subtle electronic-structure effects are responsible which are amplified or quenched depending on dopand during alloying. Small amounts of alloying with appropriate neighboring elements, as explained above, are able to fully restore the bcc phase and remove the anomalous tendency towards distortion.

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### Figure Captions.

Figure 1. Calculated (FPLMTO) pressure dependence of the shear elastic constant in V, Nb, and Ta.

Figure 2. Calculated (EMTO-CPA) total energy (at the atomic volume  $\Omega_0 = 8.056 \text{ \AA}^3$ ) as a function of the rhombohedral deformation parameter  $\delta$  (see [6] for explanation). The undistorted ( $\delta = 0$ ) crystal corresponds to the bcc phase. The curves for  $V_{95}Ti_{05}$ ,  $V_{95}Cr_{05}$ , and  $V_{95}Nb_{05}$  alloys are shifted apart 50  $\mu\text{Ry}$  for a better display of the results.

Figure 3. A select part of the Periodic Table showing the Group IVB, VB, and VIB metals. The arrows indicate alloying that causes softening of the elastic shear constant and possible destabilization of the bcc phase.

## Tables.

Table 1. Contributions to the total-energy change ( $\Delta E_{tot}$ ) due to a 1 % monoclinic deformation for vanadium and its alloys.

Material	$\Delta E_I$ (mRy)	$\Delta E_M$ (mRy)	$\Delta E_{tot}$ (mRy)
V	-0.2010	0.1820	-0.0190
V <sub>95</sub> Nb <sub>05</sub>	-0.1951	0.2102	0.0151
V <sub>95</sub> Ti <sub>05</sub>	-0.2130	0.1895	-0.0235
V <sub>95</sub> Cr <sub>05</sub>	-0.1887	0.1823	-0.0064

Table 2. The calculated charge transfer induced on the V atoms in V-M alloys.

V-Ti (0.077)	V-V (0.000)	V-Cr (-0.070)
V-Zr (0.290)	V-Nb (0.247)	V-Mo (0.196)
V-Hf (0.306)	V-Ta (0.296)	V-W (0.277)

Table 3. Contributions to the total-energy change ( $\Delta E_{tot}$ ) due to a 1 % monoclinic deformation for niobium and its alloys.

Material	$\Delta E_I$ (mRy)	$\Delta E_M$ (mRy)	$\Delta E_{tot}$ (mRy)
Nb	-0.0860	0.1930	0.1070
Nb <sub>95</sub> Zr <sub>05</sub>	-0.1200	0.1881	0.0681
Nb <sub>95</sub> Mo <sub>05</sub>	-0.0808	0.1910	0.1102

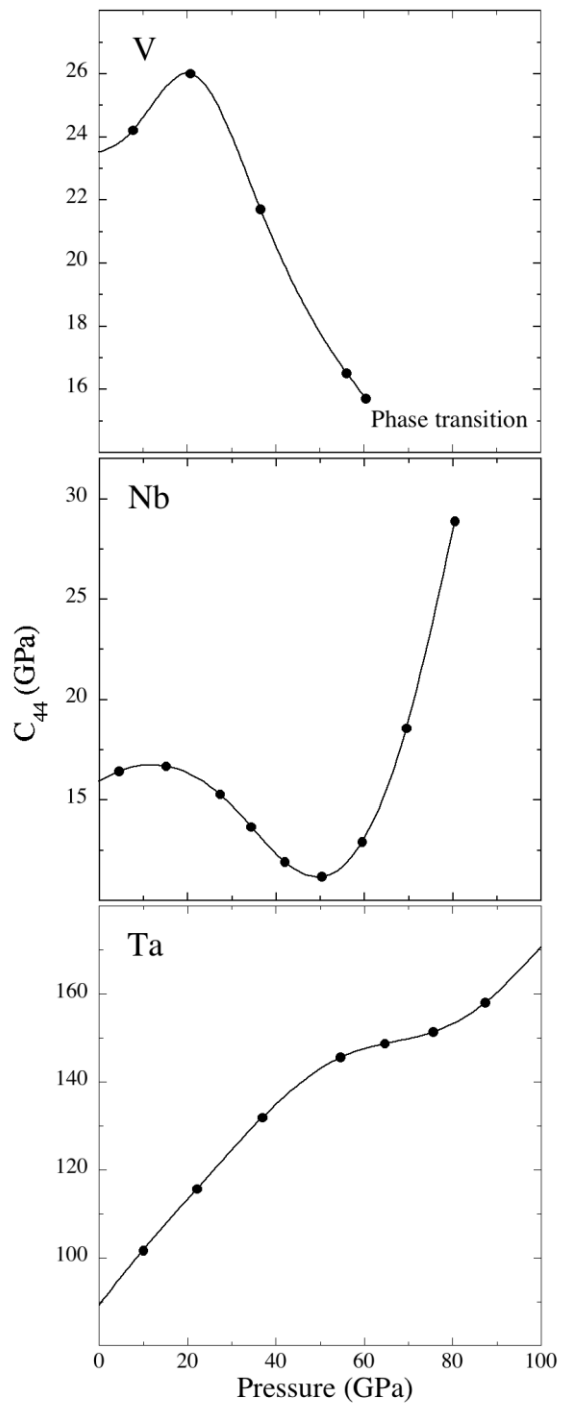


Figure 1.

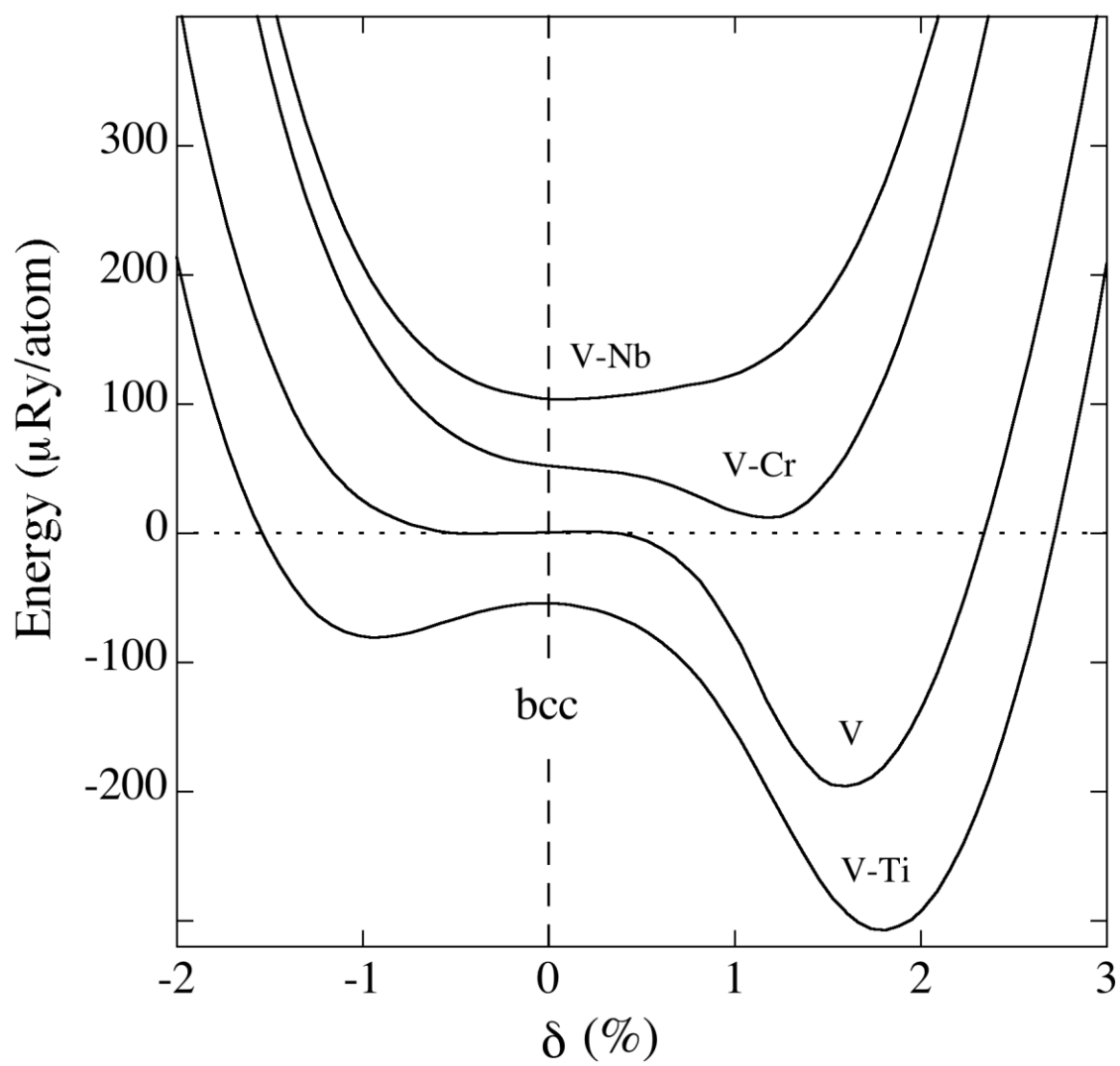


Figure 2.

<b>Ti</b> hcp	← <b>V</b> bcc	<b>Cr</b> bcc
<b>Zr</b> hcp	← <b>Nb</b> bcc	<b>Mo</b> bcc
<b>Hf</b> hcp	← <b>Ta</b> bcc	<b>W</b> bcc

Figure 3.